Hydrogen shuttling: synthesis and reactivity of a 14-electron iridium complex featuring a *bis*(alkyl) tethered N-heterocyclic carbene ligand

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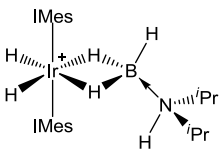
Supporting Information

General details of synthetic procedures and instrumentation

Materials: All reactions involving air- or moisture-sensitive compounds were carried out under an inert atmosphere by using Schlenk-type glassware or in a glovebox. Solvents were dried using an MBraun SPS800 prior to use. NMR-solvents were dried over molecular sieves and degassed before use when necessary. Solid starting materials were dried under high vacuum before use when necessary. Unless otherwise noted, all starting materials were commercially available and were used without further purification. $Ir(IMes)_2(H)_2Cl$ (**1**), $Na[BAr^f_4]$ and $^iPr_2NH{\cdot}BH_3$ were prepared via literature routes;[s1-s3] $Me_3N{\cdot}BH_3$ was supplied by Sigma Aldrich.

Techniques: The following instruments were used for physical characterization of the compounds: IR: Nicolet Magna-IR 560; NMR: Bruker AVC500 (^{1}H: 500 MHz; ^{13}C: 125 MHz); Bruker DRX500 (^{11}B: 160 MHz), Varian Unity500 (^{1}H: 500 MHz; ^{13}C: 125 MHz, ^{11}B: 160 MHz), Varian Mercury VX-300 (^{31}P: 122 MHz, ^{19}F: 282 MHz, ^{11}B: 96 MHz). Mass spectra were measured by the EPSRC National Mass Spectrometry Service Centre, Swansea University. Elemental microanalysis was carried out at London Metropolitan University. For all crystallographic studies, diffraction data were collected at 150 K using an Enraf Nonius Kappa CCD diffractometer;[s4] structures were solved with SIR92,[s5] or SuperFlip,[s6] and refined using the CRYSTALS software suite,[s7] as per the information contained in the CIF.

Syntheses and characterizing data for new compounds



2: To a mixture of **1** (0.43 g, 0.51 mmol) and $Na[BAr^f_4]$ (1.0 equiv.) in THF (50 mL) at -30°C was added excess $iPr_2NH{\cdot}BH_3$ (20 equiv.) and the reaction mixture warmed to room temperature, with stirring, over a period of 1 h. After a further 12 h at room temperature the resulting deep yellow solution was filtered, concentrated in *vacuo* and very light yellow crystals suitable for X-ray diffraction obtained by layering with pentane and storage at room temperature. Isolated yield 0.19 g, 21 %.

Spectroscopic data: ^{1}H NMR (300 MHz, toluene-d_8, 20°C): δ_H -21.12 (s, 2H, IrH), 0.49 (br, 3H, BH_3), 0.82 (d, $^3J_{HH}$ = 6.9 Hz, 12H, CH_3 of ^{i}Pr), 1.71 (s, 24H, *ortho*-CH_3 of IMes), 2.28 (s, 12H, *para*-CH_3 of IMes), 2.88 (m, 2H, CH of ^{i}Pr), 3.41 (br s, 1H NH), 6.74 (s, 4H, NCH of IMes), 6.81 (s, 8H, *meta*-CH of IMes), 7.47 (s, 4H, *para*-CH of $[BAr^f_4]^-$), 7.63 (s, 8H, *ortho*-CH of $[BAr^f_4]^-$). ^{13}C NMR (126 MHz, toluene-d_8, 20°C): (i) signals due to cation: δ_C 18.8 (*ortho*-CH_3 of IMes), 21.5 (CH_3 of ^{i}Pr), 24.5 (*para*-CH_3 of IMes), 49.9 (CH of *i*Pr), 122.7 (NCH of IMes), 129.8 (*ortho*-C of IMes), 137.3 (*meta*-CH of IMes), 139.5 (*para*-C of IMes), 157.8 (*ipso*-C of IMes), 170.8 (carbene quaternary of IMes); (ii) signals due to $[BAr^f_4]^-$ anion: 118.0 (s, *para*-CH), 124.8 (q, $^1J_{CF}$ = 271.8 Hz, CF_3), 129.5 ($^2J_{CF}$ = 32.7 Hz, *meta*-C), 135.4 (*ortho*-CH), 162.7 (q, $^1J_{CB}$ = 50.2 Hz, *ipso*-C). ^{11}B NMR (96 MHz, toluene-d_8, 20°C): δ_B 6.4 (br, BH_3), -6.1 ($[BAr^f_4]^-$). ^{19}F NMR (282 MHz, toluene-d_8, 20°C): δ_F -62.9. Elemental microanalysis: (calc. for $C_{80}H_{80}N_5IrB_2F_{24}$) C, 53.94; H, 4.53 N, 3.93; (meas.) C, 54.06; H, 4.48; N, 4.02.

Crystallographic data: $C_{80}H_{80}N_5B_2F_{24}Ir$, M_r = 1781.3, triclinic, $P\bar{1}$, a = 12.4528(1), b = 16.8943(2), c = 19.4968(2) Å, α = 84.630(1), β = 87.249(1), γ = 89.442(1)°, V = 4079.0(1) Å^3, Z = 2, ρ_c = 1.45 Mg m^{-3}, T = 150(2) K, λ = 0.71073 Å. 30117 reflections collected, 18572 independent [R(int) = 0.032], which were used in all calculations. R_1 = 0.0475, wR_2 = 0.1028 for observed unique reflections [$F^2 > 2\sigma(F^2)$] and R_1 = 0.0631, wR_2 = 0.1100 for all unique reflections. Max. and min. residual electron densities 2.35 and –1.47 e Å^{-3}. CSD ref.: 840395

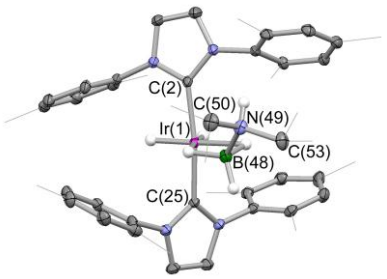
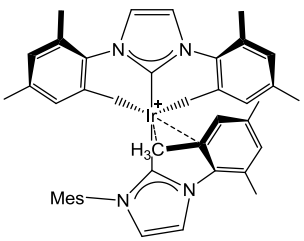


Fig. S1 Molecular structure of the cationic component of **2**; mesityl methyl groups shown in wireframe format for clarity and thermal ellipsoids set at the 40% probability level.



5: To a suspension of $Na[BAr^f_4]$ (1.06 g, 1.19 mmol) in THF (50 mL) at -30°C was added **1** (1.0 equiv.) and the reaction mixture warmed to room temperature over 1 h. After stirring for a further 48 h, the resulting deep red solution was filtered, concentrated *in vacuo* and bright red crystals suitable for X-ray diffraction obtained by layering with pentane and storage at room temperature. Isolated yield 1.54 g, 78 %.

Spectroscopic data: ^{1}H NMR (300 MHz, dichloromethane-d_2, 20°C): δ_H 1.82 (s, 6H, *ortho*-CH_3 of IMes"), 1.88 (s, 6H, *para*-CH_3 of IMes"), 1.94 (s, 24H, *ortho*-CH_3 of IMes), 2.28 (s, 12H, *para*-CH_3 of IMes), 2.32 (br, 2H, CH_2 of IMes"), 2.42 (br, 2H, CH_2 of IMes"), 6.80, 6.88 (s, 4H, NCH of IMes and IMes"), 6.90 (s, 2H, *meta*-CH of IMes"), 7.05 (s, 4H, *meta*-CH of IMes), 7.31 (s, 2H, *meta*-CH of IMes"), 7.47 (s, 4H, *para*-CH of $[BAr^f_4]^-$), 7.63 (s, 8H, *ortho*-CH of $[BAr^f_4]^-$). ^{11}B NMR (96 MHz, toluene-d_8, 20°C): δ_B -6.1. ^{19}F NMR (282 MHz, toluene-d_8, 20°C): δ_F -62.7. Elemental microanalysis: (calc. for $C_{74}H_{58}N_4BF_{24}Ir$) C, 53.44; H, 3.52; N, 3.37; (meas.) C, 53.75; H, 3.63; N, 3.18.

Crystallographic data: $C_{74}H_{58}N_4BF_{24}Ir$, M_r = 1662.3, monoclinic,

$P\ 2_1/c$, a = 16.9900(2), b = 20.4349(2), c = 21.0342(3) Å, β = 104.898(1)°, V = 7057.4(2) Å^3, Z = 4, ρ_c = 1.56 Mg m^{-3}, T = 150(2) K, λ = 0.71073 Å. 31364 reflections collected, 16000 independent [R(int) = 0.039], which were used in all calculations. R_1 = 0.0440, wR_2 = 0.0854 for observed unique reflections [$F^2 > 2\sigma(F^2)$] and R_1 = 0.0662, wR_2 = 0.0923 for all unique reflections. Max. and min. residual electron densities 2.04 and –1.13 e Å^{-3}. CSD ref.: 840397.

References

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